

LITHIUM ANODE
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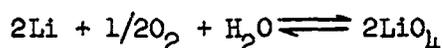
The application of lithium as anode in a metal-air battery can only be conceived using an aprotic media. If one refers to organic aprotic solvents as the aprotic electrolyte there is not any doubt that Li is the most popular and promising anode available. It is also well known the considerable government effort in the development of high energy organic electrolyte batteries which practically in any case include Li as the postulated anode. In fact, Li has a very low equivalent weight of 6.9 and it should produce one of the lightest weight practical anodes. In addition, it has a high equivalent potential of around -3 volts dependent of the electrolyte used. The electrode has been found to be reversible in several electrolytes. For example, potentiometric studies in LiCl-Dimethylformamide (DMF) showed that the potential obeys the Nernst equation over a wide concentration range, between $10^{-4} < C < 1F$. The relationship between current and potential for Li electrodes has been measured under steady-state conditions in a number of different electrolytes. In general, it has been found that the polarization of this electrode is small and apparently it is more related with the solvent than with the solute. The exchange current density for Li was measured in electrolytes containing, PC (propylene carbonate), BL (butyrolactone), DMF (dimethylformamide), DMSO (dimethyl sulfoxide), and PC-NM (nitro methane) mixtures. The value was in the order of 1 ma/cm^2 which is a quite high exchange current value and supports the reversibility of this anode. A number of electrode configurations are being considered in the development of test cells. The methods of electrode preparation have included the following:

- a. Pressing or rolling Li ribbon onto metal screen made of copper, silver, nickel and aluminum.
- b. Pressing lithium powder with or without conducting additives onto metal screens.
- c. Dipping nickel screen into molten lithium. Apparently the former method is the one which has given better results in terms of least polarization and highest efficiency.

Research in primary systems has shown that the coulombic efficiencies of lithium anodes are in general very high; they vary between 70-100%. Relative high current densities have been sustained on Li electrodes, for example, 30 ma/cm^2 is quite normal and relatively easy to achieve; values up to 100 ma/cm^2 were also reported. Considerable work has been done on the possibilities of Li in secondary batteries. The reported data are promising, but at best the cycling efficiency for lithium electrodes appears to be about 85%. There is a clear tendency to decrease as the number of cycles increases. The reasons for low cycling efficiency are not entirely understood, however, the processes most likely responsible may be: mechanical loss of electrodeposit Li; loss of electrical contact during anodic discharge due to a

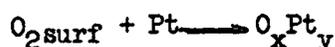
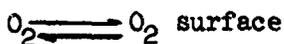
preferential attack at the base of Li dendrites; alloy formation with the substrate material or occurrence of side reactions which would not produce electricity. It should be pointed out here that practically all the work reported about Li oxidation was done with solvents which in few of the best cases had approximately 50 ppm of water, but in general were much more contaminated with it. Concentrations of 500-1000 ppm were very frequent. These quantities appear to exert minor effect on the discharge of Li, but the reasons are not clearly understood yet because water may form lithium hydroxide which can passivate the electrode.

Related with the development and possibilities of the couple Lithium-Air the only source available under my knowledge is a contract performed by Globe-Union between March 1966 to June 1967 with USA Mobility Equipment Research and Development Center, Fort Belvoir, Va. The intention of the contract was the analysis of the couple in order to develop a high energy secondary battery. Unfortunately the contract was not continued enough to permit a complete evaluation of the system. During the contract period a major emphasis was imposed on the behavior of the air electrode in organic electrolyte and only initial data was obtained about the negative electrode. The reason of this priority was that at that time very little was known about the kinetics of O₂ reduction in aprotic solvents in opposition of a fairly large volume of data related with the Li anode. The postulated couple included also water as moisture and the system was called Lithium-moist Air Battery. The induction of water was postulated in order of the Li tolerance of water a. with the intention to transform the oxygen reduction products in hydroxide and also permit the formation of LiOH which was considered insoluble and should be formed on the anode surface. This last picture would help the development of a secondary battery. The overall expected reaction was

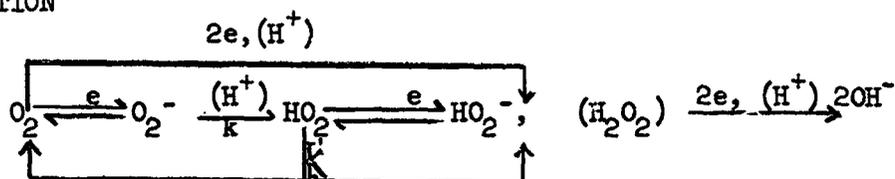


The research was carried out principally on one solvent, NDA, nitrosodimethylamine, an interesting aprotic solvent, but with very toxic properties. The experimentation was performed using two solutes: LiClO₄ and a tetra substituted ammonium compound; phenyl-trimethyl ammonium hexafluorophosphate (PhMe₃ NPF₆). The study of oxygen reduction turned out to the postulation of a very complex mechanism which included first, a series of surface processes on the electrode (adsorption, interaction between oxygen and platinum, reduction of the film formed) and second two partially mass transport dependent steps with chemical kinetics complication (E.C.E.). Superoxide and peroxide were postulated as intermediates:

SURFACE PROCESS



OXYGEN REDUCTION



PIC-BAT 209/11

The effect of increasing water concentration was studied in detail and it showed that the overall mechanism of oxygen is very much affected by water availability. Apparently a reaction similar to the one in aqueous media occurs only at H₂O concentration over 1%. At this concentration the current capabilities achieve also a maximum value.

During the last part of the contract few experiments were run in order to test the compatibility of the overall system. Initial experiments using the electrolyte PhMe₃NPF₆-NDA showed that the air electrodes can support current densities up to 20-30 ma/cm² while Li independently, in the same electrolyte, was discharged at 30 ma/cm². The whole system using small laboratory scale cells was discharged at low current densities (2-5 ma/cm²) for short time. Apparently there is compatibility of anode and cathode and a 2 volt battery might be possible.

From these data some ideas can be postulated about the possible development of the battery. The minimum level of water concentration for full current capabilities of the O₂ electrode is too high for the behavior of the Li anode. This problem would require the development at lower concentration of water with the consequent decrease in current capabilities of the air electrode and the possibility of building up superoxide and peroxide compounds. Engineering design may permit a separation of catholyte and anolyte in order to allow the behavior of each electrode at different water concentration.